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Halogen-free flame-retarded polyester composition

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HALOGEN-FREE FLAME-RETARDED POLYESTER COMPOSITION

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The invention relates to a halogen-free flame-retarded polyester composition, more specifically to such composition comprising melamine cyanurate as flame-retardant additive. The invention also relates to a moulded part for use in electrical or electronic applications comprising said polyester composition.

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Polyester compositions, more specifically thermoplastic polyester compositions, are often used in applications that have non-flammability properties as a critical requirement. Typical examples are parts for use in various electrical or electronic appliances, like housings, bobbins, switches and connectors. Depending on the specific application, the polyester composition should fulfil various

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requirements regarding desired mechanical and electrical properties of parts moulded therefrom. In many of these applications the polyester compositions should be classified as V-0 in the flame retardancy test according to Underwriter's Laboratories Standard 94 vertical (UL-94 V test), which is one of the most stringent requirements. For use in for example connectors or bases for energy-saving

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lamps, which often are rather thin walled, the polyester composition should for example display sufficiently high stiffness and strength and yet have enough ductility, have good stability during moulding and good melt flow behaviour to ensure complete mould filling at short cycle times. The moulded part should show a.o. good dimensional and heat stability, e.g. during use at higher temperatures. In

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order to comply with all these different requirements a polyester composition generally contains a series of components, like flame-retardant compounds, anti-dripping agents, flow promoters, reinforcing agents, impact-modifiers, release agents, stabilizers, colorants, and laser-marking additives.

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A complicating factor is that halogenated, especially brominated flame-retardants should not be used anymore in view of their environmental effects, and legislative developments. Especially for polyester compositions it appears very difficult to find alternative halogen-free flame-retardant systems.

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Halogen-free flame-retarded polyester compositions comprising melamine cyanurate as flame-retardant additive have been described in numerous publications. Melamine cyanurate is the name commonly used for the 1:1 adduct of melamine (2,4,6-triamino-1,3,5-triazine) and cyanuric acid (2,4,6-trihydroxy-1,3,5-

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triazine) or its tautomer.

Such a halogen-free flame-retarded polyester composition is known from for example EP 0899296 A2. In this patent application a poly(butylene terephthalate) (PBT) composition comprising 30% melamine cyanurate is disclosed, which shows a V-2 rating in the UL-94 test at 1.6 mm sample thickness. A V-0 rating in said test is reported for a PBT composition comprising 5% melamine cyanurate and 10% of the aluminium salt of 1-hydroxy-3-methyl-1H-phospholane-1-oxide.

In US 4,180,496 PBT compositions comprising 20 and 30 mass% melamine cyanurate are disclosed that would show improved flame-proofing, but UL-94 classification is not given. It is furthermore indicated that higher levels of melamine cyanurate in a polyester polymer would be disadvantageous for its properties.

Many later publications report improvement of flame-retardancy and mechanical properties of polyester compositions comprising up to about 20 mass% melamine cyanurate, in most cases in combination with a further auxiliary flame-retardant component and a reinforcing agent like glass fibres. JP 3-281652 A, for example, discloses polyester compositions comprising melamine cyanurate and a phosphate or phosphonate compound as flame-retardant combination, and fillers. In JP 6-157880 reinforced poly(alkylene terephthalate) compositions comprising melamine cyanurate and a P-containing compound are described. EP 1024167 A1 discloses glass-fibre reinforced PBT compositions with melamine cyanurate and an aluminium- or zinc phosphinate. In both WO 01/81470 A1 and WO 03/002643 A1 flame-retarded polyester compositions are disclosed that contain melamine cyanurate, a zinc and/or boron compound, and a phosphorous-containing compound as flame-retardant system.

The known compositions still show some disadvantages, in that for example processing behaviour is troublesome, colour or colour stability is unsatisfactory, or thermal or hydrolysis resistance is reduced, for example by P-containing compounds. In most instances, the disclosed compositions cannot be classified V-0 in the UL-94 test. Another disadvantage is that some additional compounds significantly add to the cost-price of the composition.

There is thus still a need in industry for a halogen-free flame-retarded polyester composition that combines non-flammability (preferably UL-94 V-0 classification) with sufficiently high stiffness, good moulding behaviour, and a low cost-price.

According to the present invention, this is provided by a halogen-free flame-retarded polyester composition comprising

- (A) 30-65 mass % of at least one thermoplastic polyester polymer;
 - (B) 35-50 mass % melamine cyanurate;
 - 5 (C) 0-15 mass % other polymers; and
 - (D) 0-10 mass % other additives;
- and wherein the sum of components (A) – (D) totals 100 mass %.

10 The polyester composition according to the invention fulfils the UL-94 V-0 requirements at 1.6 mm, shows good moulding behaviour, higher stiffness without using glass fibres, relatively low density, a light natural hue and good colourability; and is suited for making parts for use in electrical or electronic applications, like for example lamp bases of energy-saving lamps. Such parts release no or very little hazardous fumes and smoke when exposed to fire, for example a low amount of carbon monoxide.

15 The at least one thermoplastic polyester polymer (component A) in the polyester composition according to the invention generally forms a continuous phase of the composition, and is preferably a semi-crystalline polyester. Said polyester is generally derived from at least one aromatic dicarboxylic acid or an ester-forming derivative thereof and at least one (cyclo)aliphatic or aromatic
20 diol, and includes homo- as well as copolymers. Examples of suitable aromatic diacids include terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, biphenyl dicarboxylic acid, etc., with terephthalic acid being preferred. Suitable diols include for example alkylene diols, hydroquinone, dihydroxyphenyl, naphthalenediol. Alkylene diols, like ethylene diol, propylene diol, 1,4-butylene diol
25 or butane diol, neopentylene diol, and cyclohexane dimethanol are preferred. A special class is formed by polyesters containing long chain diols, like poly(alkylene oxide) diols, aliphatic polyester diols or aliphatic polycarbonate diols in addition to other said diols. This last group of polyesters, including so-called polyether esters and polyester esters, is also referred to as segmented blockcopolyesters.
30 Depending on the amount of long chain diol in such polyester, the material can be a stiff but tough plastic or flexible thermoplastic elastomer. The polyester may further comprise a small amount of a branching component, i.e. a compound containing three or more ester-forming groups, to affect melt rheology. Said polyesters and their preparation are for example described in 'Encyclopedia of
35 polymer science and technology', Vol. 12, John Wiley & Sons, New York, 1988 (ISBN 0-471-80944-6).

In a preferred embodiment the thermoplastic polyester is a poly(alkylene terephthalate), like poly(ethylene terephthalate) (PET), poly(1,4-butylene terephthalate) or simply called poly(butylene terephthalate) (PBT), poly(propylene terephthalate) (PPT), poly(cyclohexane terephthalate) (PCT), or
5 copolymers thereof with a minority content of another dicarboxylic acid or diol. Preferably, the content of other monomers in these polyesters is below 30, below 20, more preferably below 10 mol% to ensure semi-crystalline properties. Also blends of different types or grades of poly(alkylene terephthalates) can be used. These polyester compositions are very suited for use as moulding compositions,
10 especially as injection-moulding compositions.

In a special embodiment according to the invention the composition contains a poly(butylene terephthalate) as the polyester. Advantages thereof include easy processing during compounding and injection-moulding, while moulded parts still have sufficient thermal resistance. The relatively low processing
15 temperatures of PBT allow a broader choice of additives, and help to prevent excessive degradation. The composition may also contain another polyester, e.g. PET, in minority content. Such a PBT/PET polyester blend has advantages regarding processing, and results in moulded parts with better surface appearance.

In another special embodiment according to the invention the composition contains a poly(butylene terephthalate) containing long chain diols as the polyester. Advantages thereof include easy processing during compounding and injection-moulding, and a relatively high toughness, e.g. elongation at break of the composition and parts moulded therefrom. The amount of long chain diol is such that the PBT blockcopolyester has a hardness in the range of about 25-75
25 Shore D; preferably about 35-70 Shore D.

Specifically preferred is a composition containing poly(butylene terephthalate) having a relative solution viscosity of 1.7-2.5, or 1.8-2.2 (as measured on a 1 mass % solution in m-cresol at 25°C). The advantage thereof is favourable melt-flow behaviour of the polyester composition, and sufficient
30 mechanical properties, e.g. stiffness and toughness, to make thin-walled structural parts.

The composition according to the invention contains 35-50 mass% of melamine cyanurate as flame-retardant additive (component B), in fact as the sole flame-retardant additive. Melamine cyanurate is the name commonly
35 used for adducts or salts of melamine (2,4,6-triamino-1,3,5-triazine) and

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(iso)cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine or its tautomer), as described in for example US 4,180,496. Lower amounts of melamine cyanurate appeared not to result in the desired V-0 classification, whereas still higher amounts only reduce mechanical properties and processability of the composition. The melamine

5 cyanurate is preferable of small particle size, or can be easily dispersed into small particles in a polyester continuous phase during mixing. Suitable melamine cyanurate has a particle size distribution with 50% of the particles (d50) smaller than about 50 micrometer (μm), preferably particle size is below 25, below 10, or even below 5 μm . The melamine cyanurate particles may have been provided with

10 an organic or inorganic coating, to improve its performance, for example dosing behaviour, or dispersibility. Preferably, the composition comprises 37-45, or even 38-42 mass% of melamine cyanurate.

In contrast to many compositions described in the art, the composition according to the invention is substantially free from phosphor-

15 containing compounds as flame-retardant additive. Although the composition may comprise minor amounts of P-containing compounds as for example a stabilizer, the composition according to the invention is substantially free from phosphor; preferably the P-content is below 0.1, 0.05 or even below 0.02 mass%.

The composition according to the invention may further contain

20 0-15 mass % other polymers (component C), like amorphous polymers and/or impact-modifiers. Suitable amorphous polymers include styrenic and acrylic polymers, polycarbonates, especially aromatic polycarbonates, and mixtures or copolymers thereof. The amorphous polymer preferably has a glass transition temperature (T_g) higher than the T_g of the polyester polymer. Preferred polymers

25 include thermoplastic polymers of styrene, alpha-methylstyrene, methyl acrylate, methylmethacrylate, acrylonitrile, methacrylonitrile, maleic acid anhydride, N-substituted maleimide, vinyl acetate, or mixtures thereof. Preferred polycarbonates are aromatic polycarbonates prepared from a dihydric phenol and a carbonate precursor, including copolymers like polyester carbonates. Most preferred is the

30 polycarbonate derived from bisphenol A and its copolymers, generally simply called polycarbonate. As impact-modifier generally rubbery materials are used, preferably consisting of or comprising functionalized copolymers that are compatible with or reactive towards the polyester and having a T_g below ambient temperature, preferably below 0, -20 or even below -40°C. Suitable examples

35 include styrenic, olefinic or (meth)acrylic copolymers with acid, acid anhydride-, or

epoxy functional groups, like a copolymer of ethylene, methylmethacrylate and glycidyl methacrylate or a maleicanhydride-functionalized copolymer of ethylene and propylene. Also suitable are acrylonitrile butadiene styrene copolymers (ABS), styrene butadiene styrene copolymers (SBS) or hydrogenated versions thereof
5 (SEBS), methacrylate butadiene styrene (MBS), or core-shell polymers having an acrylate rubber core and a shell comprising a vinyl aromatic compound and/or a vinyl cyanide and/or an alkyl(meth)acrylate. An effective amount of impact-modifying polymer is generally about 5-20 parts per 100 parts of PBT; that is the composition preferably comprises about 2-10 mass% of said other polymers.

10 During evaluation of flammability behaviour according to the UL-94 test, dripping of molten polyester composition during flaming may prevent a V-0 classification. To prevent dripping, typically upto 2 mass % of fibrillating polytetrafluoroethylene (PTFE) is generally added in the art as anti-dripping agent to a flame-retarded composition. Surprisingly, it was found that upon adding PTFE
15 the polyester composition did not classify as V-0 anymore. The other polymers mentioned above therefore do preferably not include PTFE and the like; and the composition according to the invention is preferably substantially free of fluorine polymers like polytetrafluoroethylene; making these compositions truly halogen-free (except perhaps for some traces or minor amounts present in other additives).

20 The composition according to the invention may further contain 0-10 mass % of other additives (component D). Examples of additives include inorganic fillers, plasticisers, processing aids, stabilizers, anti-oxidants, agents that improve electrical properties, dispersing aids, colorants, laser-marking additives, etc..

25 Preferably, the composition according to the invention does not contain fibrous reinforcing agents like glass fibers, since these were found to deteriorate the desired V-0 classification. Fibrous reinforcing agents are herein understood to mean elongate particles having a length much greater than its dimensions in transverse directions and having an aspect ratio, that is the ratio of
30 length to thickness, of at least 10. In order to obtain a polyester composition with desirable combinations of strength, stiffness, elongation at break and impact resistance values, the composition may comprise other polymers (component C), and/or inorganic filler materials, for example inorganic fillers like glass beads, silica, (calcined) clay, mica, talc, kaolin, wollastonite, metal oxides, etc.. These filler
35 materials can have various forms, including globular, platelet or needle-like shapes. If the filler is needle-like or fibrous, its aspect ratio is preferably below 10.

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or below 8.

Processing aids include e.g. mould-release agents, lubricants, nucleating agents, and flow-promoters. Stabilizers for example include thermo-oxidative stabilizers like hindered phenolic compounds, hydrolysis stabilizers, such as acid scavengers like carbodiimides and epoxy compounds, and UV-stabilizers. Apolar polymers like polyolefines, and inert fillers like bariumsulphate may be added to improve for example the comparative tracking index or other electrical properties of the composition. The type and amount of colorants like inorganic pigments and organic pigments or dyes is chosen such that it does not deteriorate other properties. Inorganic filler, metal oxides, or other colorants may also be present to improve contrast upon irradiation with a laser-beam.

The polyester composition according to the invention can be prepared in any customary manner by blending the various components in a suitable mixing device. Preferred devices are extruders, especially twin-screw extruders, most preferably with co-rotating screws. In a preferred method, the polyester and other polymers are dosed to the first feed port and melamine cyanurate, optionally pre-blended with other additives, downstream. The advantage thereof is better control over the maximum temperature during compounding, and better dispersing of components into the polyester.

In a special embodiment, the composition is subjected to a heat-treatment after mixing or compounding, preferably at a temperature close to but below the melting point of the polyester polymer, and under reduced pressure or a flow of an inert gas. This heat-treatment will increase the molar mass and the relative viscosity of the polyester in the composition (also referred to as solid-state postcondensation), and improve mechanical properties of the composition.

The invention also relates to a moulded part for use in electrical or electronic applications, which part comprises the polyester composition according to the invention. Preferably such a part is made via injection moulding techniques.

The invention also provides an article, like an electrical or electronic appliance, comprising a part moulded from a polyester composition according to the invention. A typical example is an energy saving lamp comprising a lamp base made from the polyester composition according to the invention.

The invention will now be further illustrated by means of the following examples and comparative experiments.

Example 1

As starting components following materials were applied:

- PBT polymer with relative solution viscosity (RSV) of 1.98 (as measured on 1 mass % solution in m-cresol at 25°C, based on ISO 307); and 52 meq/kg of carboxylic end-groups (Ec);
- Melapur® MC XL, a compacted melamine cyanurate, available from Ciba Specialty Chemicals;
- Pentaerythritol tetrastearate (Radia® 7176) mould release agent (at 0.25 mass% of total composition).

The composition was prepared on a Berstorff ZE25 twin-screw extruder. Barrel temperatures were set at room temperature for the first 6 zones, and at 270°C for zones 7-11 and die head. Throughput was about 30 kg/h, and screw-speed 350 rpm. PBT pellets were dosed to zone 1, a powdery mixture of melamine cyanurate and mould release agent was dosed via a side-feeder to zone 5. Vacuum degassing was applied on zone 10. A single extruded strand was cooled in water and granulated. Observed temperature of the melt was 315°C at maximum.

Test specimen were injection moulded from granulate, pre-dried during 10 hrs at 120°C to a water content below 0.02 mass%, on an Engel 80A machine, with standard temperature settings for PBT. Standard test bars were made in accordance with UL-94, ISO 527, or ISO 179.

Flammability behaviour was tested according to the UL-94 vertical burning test, using test bars of 1.6 mm thickness. Before testing samples were conditioned at 23°C, 50% RH for 48 hours; or aged at 70°C during 168 hrs.

Tensile properties were measured according to ISO 527/1A. Charpy impact was tested according to ISO 179/1eU. HDT-A was determined according to ISO 75/A at 1.8 MPa.

Examples 2 and 3.

Analogously to Ex. 1 compositions were made from PBT polymer with RSV of 1.85 and 2.10, and Ec of 32 and 21 meq/kg, respectively.

Compositions and results are collected in Table 1.

All 3 samples could be compounded and processed without difficulties into off-white test bars (typical values for L*, a* and b* are in the ranges 89-91, 0.8-1.2, and 10-11, respectively), and show a V-0 classification for both

series of samples (conditioned at 23° and 70°C). The PBT polymer shows some loss in molar mass after compounding, but no increase in carboxylic acid end-groups. The materials show higher stiffness than plain PBT, and although strength and toughness are relatively low, the materials are suited for making thin-walled parts having flame-retardance and sufficient dimensional strength and stability. A higher molar mass of PBT results in a tougher composition.

Comparative experiments A-G

In these experiments the melamine cyanurate content of the composition was lowered, or some glass fibres (as chopped glass fibres with sizing agent suitable for polyesters), and/or a small amount of PTFE (Dyneon TF1654) was added. During sample preparation the PTFE was together with other components dosed at zone 5, whereas glass fibres were dosed downstream onto the melt at zone 8. Other conditions and evaluations were analogous to Examples 1-3; except for samples E and F wherein throughput was lowered such that the temperature of the melt remained below about 315°C.

From the data collected in Table 1 it can be seen that lowering the melamine cyanurate content to 30 mass% results in a V-2 classification (dripping, ignition of cotton). Addition of some PTFE, known as anti-dripping additive, did not improve flammability behaviour, but in contrast results in NC classification; even for a 40% melamine cyanurate composition. PTFE did not affect other properties. Addition of 7.5 or 15 mass% glass fibres resulted in compositions with higher mechanical properties, but with UL-94 NC classification.

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Table 1

experiment		1	2	3	A	B	C	D	E	F	G
composition											
PBT/melamine cyanurate	mass ratio	6/4	6/4	6/4	7/3	7/3	6/4	6/4	6/4	6/4	7/3
glass fibres	mass%	0	0	0	0	0	0	7.5	7.5	15	7.5
PTFE	mass%	0	0	0	0	1	0.5	0	1.0	0.5	0.5
properties											
RSV		1.82	1.72	1.89	1.87	1.81	1.78	1.75	1.72	1.71	1.80
Ec	meq/kg	51.1	26.6	23.9	50.7	51.4	52.7	51.1	54.1	52.2	52.3
UL-94 V @ 1.6 mm	class	V-0	V-0	V-0	V-2	NC	NC	NC	NC	NC	NC
Tensile modulus	MPa	5080	5037	4820	4327	4843	5254	6943	7384	9503	6543
Tensile strength	MPa	29.7	25.5	31.6	36.1	40.1	31.3	45.2	46.2	61.9	57.7
Elongation at break	%	0.6	0.5	0.7	1.0	1.0	0.7	0.8	0.7	0.8	1.2
Charpy impact	kJ/m ²	6.2	4.7	6.2	9.0	11.9	7.1	8.7	10.3	14.1	15.5
HDT-A	°C	134	143	130	128	118	130	198	199	210	199

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CLAIMS

1. Halogen-free flame-retarded polyester composition comprising:
 - (A) 30-65 mass % of at least one thermoplastic polyester polymer;
 - 5 (B) 35-50 mass % melamine cyanurate;
 - (C) 0-15 mass % other polymers; and
 - (D) 0-10 mass % other additives;and wherein the sum of components (A) – (D) totals 100 mass %.
2. Composition according to claim 1, wherein the thermoplastic polyester is a
10 poly(alkylene terephthalate).
3. Composition according to claim 1, wherein the thermoplastic polyester is
poly(butylene terephthalate).
4. Composition according to any one of claims 1-3, wherein melamine cyanurate
is the sole flame-retardant additive.
- 15 5. Composition according to any one of claims 1-4, comprising 37-45 mass% of
melamine cyanurate.
6. Composition according to any one of claims 1-5, being substantially free from
phosphor-containing compounds.
7. Composition according to any one of claims 1-6, wherein the other polymer is
20 an amorphous polymer having a glass transition temperature higher than the
polyester polymer.
8. Composition according to any one of claims 1-6, wherein the other polymer is
a rubbery impact-modifier.
9. Composition according to any one of claims 1-8, wherein the composition is
25 substantially free of fluorine polymers like polytetrafluoroethylene.
10. Moulded part for use in electrical or electronic applications, comprising the
polyester composition according to any one of claims 1-9.

ABSTRACT

The invention relates to a halogen-free flame-retarded polyester composition comprising 30-65 mass % of at least one thermoplastic polyester polymer;
5 35-50 mass % melamine cyanurate; 0-15 mass % other polymers; and 0-10 mass % other additives. The invention also relates to a moulded part for use in electrical or electronic applications comprising said polyester composition.